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Direct current dielectrophoretic manipulation of the ionic liquid droplets in water

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ABSTRACT

The ionic liquids (ILs) as the environmentally benign solvents show great potentials in microemulsion carrier systems and have been widely used in the biochemical and pharmaceutical fields. In the work, the ionic liquid-in-water microemulsions were fabricated by using two kinds of hydrophobic ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] and 1-Hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] with Tween 20. The ionic liquid droplets in water experience the dielectrophoretic (DEP) forces induced by applying electrical field via a nano-orifice and a micron orifice on the opposite channel walls of a microchannel. The dielectrophoretic behaviors of the ionic liquid-in-water emulsion droplets were investigated under direct current (DC) electric field. The positive and negative DEP behaviors of the ionic liquid-in-water droplets varying with the electrical conductivity of the suspending medium were investigated and two kinds of the ionic liquid droplets of similar sizes were separated by their different DEP behaviors. In addition, the separation of the ionic liquid-in-water droplets by size was conducted. This paper, for the first time to our knowledge, presents the DC-DEP manipulation of the ionic liquid-in-water emulsion droplets by size and by type. This method provides a platform to manipulate the ionic liquid droplets individually.

1. Introduction

Microemulsions are the liquid droplets, which are dispersed in an immiscible liquid and have tremendous potentials for the synthesis of nanoparticles [1], the single-cell biology [2,3], and the production of semiconductor microcolloids [4]. Due to the good biocompatibility and high solubilization capacity, the emulsion droplets can function as the carriers for the drug delivery and biochemical reactors [5,6]. Generally, the microemulsion droplets are fabricated by mixing two immiscible liquid with large-scale instruments. Currently, the microfluidics has become an alternative technique to generate emulsion droplets. According to the geometry of the microchannel in the microfluidic chip, it enables to produce the droplets with controllable sizes by using the flow-focusing and T-junction configurations [7]. However, it is still difficult to fabricate the droplets with precise size and the droplets generated by these methods have wide size distributions which is undesired. Therefore, it is essential to develop a device to achieve the size-dependent separation of the emulsion droplets and to sort the droplets in well-defined diameter with uniform morphology. Generally, the microemulsion is a system of water, oil, and amphiphiles. The water-in-oil emulsions are used for the transportation of oil-soluble drugs, while the oil-in-water microemulsions are suitable for the water-soluble ones [8]. For the applications which are impossible with the conventional water-oil microemulsions, ionic liquids (ILs) have been employed. The IL droplets have led to the development of many new applications in colloid and interface science [9]. ILs are salts with melting points below 100 °C and consist of organic cation and inorganic or organic anion [10,11]. Since they are liquid at room temperature and have excellent solubility in various organic and inorganic compounds [12], the ILs can be formulated to be hydrophobic or hydrophilic and serve as the solvents for various reactions [13]. Due to the diverse structure and unique physicochemical properties [14,15], i.e., insignificant vapor pressure and excellent biochemical stability [8,16], ILs are applied in a variety of fields such as separation [12], electrochemistry [17,18], chemical engineering [19–29] and biotechnology [30–33]. Because of the favorable physical and chemical properties of the ILs, they are proved to be excellent solvents, leading to improved separation efficiency of metal ions or biomolecules from different media [34–39]. The direct extraction of the double-stranded DNA into the IL [Bmim][PF_6] has been demonstrated [40]. The binding between the ILs and DNA was enhanced by the hydrophobic interactions between the alkyl chains of the ionic liquid and DNA, and the extraction efficiency of DNA was improved by optimizing the properties of the ILs [41]. Moreover, By

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using the hydrophobic IL [Bmim][PF_6], the gold nanoparticles and nanorods were extracted from water to BMIM-PF_6 quantitatively [42]. In order to assist the extraction process, the nanoparticles are dispersed in the ILs and various hybrid structures are produced. The nanofluid was induced for the extraction of fungicides from water by adding ZnO nanoparticles into the IL [Hmim][PF_6] [43]. The ferrofluid was utilized to extract lead and cadmium from milk and biological samples by using the [Hmim][PF_6] with titania-coated magnetite nanoparticles, leading to improved separation rate compared with conventional extraction method [44].

Because of the advantages of ILs' high separation and extraction efficiency, excellent stability, and biocompatible environment [39], the IL microemulsions are widely used for molecules storage and drug delivery. Goindi et al. [45] fabricated the IL-in-water microemulsions to act as the carriers for the delivery of the poorly water-soluble drug of etodolac and found that it was more effective to control inflammation by using the etodolac loaded IL-in-water microemulsions than the oil solution, oil-in-water microemulsions, and commercial etodolac. The IL-in-water microemulsions [8,46] were also employed to enhance the transdermal delivery of the sparingly soluble drugs and the pharmaceutical grade organic solutions. The IL-based nonaqueous microemulsions were found to be an efficient nano-delivery system and provide potential delivery carriers for the insoluble or sparingly soluble drug molecules. Nor et al. [47] demonstrated the formulation of IL-in-oil nanoemulsions with the various mass ratio between the Tween-80 and Span-20, and shown that high concentration of the Tween-80 in the nanoemulsions led to better separation and sedimentation stability. By selecting an optimized surfactant ratio, a high separation and drug encapsulation efficiency can be achieved, offering potential carriers for various drug delivery. However, among these various applications of the IL microemulsions, the dielectrophoretic manipulation of IL-in-water emulsion droplets has not been explored.

Dielectrophoresis refers to the induced motion of the particles/droplets in an aqueous solution under a non-uniform electric field. The non-uniformity of the electric field can be formed by employing alternative current (AC) electric fields to an array of the microelectrodes embedded inside the microchannel and by employing DC electric fields through the external microelectrodes via the electrically constricted microfluidic channel. Since each kind of droplet or particle shows a unique electrical property, AC-DEP is widely utilized to identify and separate the particles by adjusting the frequency of the applied AC electric field. Generally, in the conventional electrode-based AC-DEP systems, the fabrication of the microelectrodes is expensive and time-consuming [48,49], and the experimental set-up is complicated [50,51]. By using the liquid metal to fabricate the microelectrodes instead of the traditional solid electrodes, the complicated fabrication steps are avoided and it facilitates the creation of the electrodes with various structures and dimensions in the desired pattern and structure [52,53]. However, the chemical reactions and fouling of microelectrodes are still involved [54]. In this study, by employing a novel asymmetric orifice based DC-DEP microfluidic chip, these problems can be overcome. To produce the electric field gradient, the DC electric voltages are employed through the external electrodes across a nano orifice and a micron orifice [7,55–57]. By choosing a large width ratio of the asymmetric orifices, a stronger non-uniformity of the electric field and hence the large DEP forces can be induced, resulting in a high separation resolution, such as the size-dependent separation of smaller silicone oil droplets (7.5 μm and 11 μm in diameter) with a size difference of only 3.5 μm [7]. By choosing the surrounding medium with a specific electrical conductivity, a high separation sensitivity was achieved, such as the separation of micron polystyrene particles by 2 μm size difference and nanoparticles with only 10 nm size difference [55,56]. Therefore, it can be expected that the resolution of separating droplets by size by this method can be significantly improved. In the future, we will continue to optimize our chip design to achieve higher separation sensitivity and resolution. Moreover, by using the pressure-driven flow, the movement of the particles or droplets can be easily controlled and the throughput can be dramatically increased. Furthermore, since these droplets are exposed to the electric field gradient only when passing through the dielectrophoretic manipulation area, there will be no aggregation of the droplets and transporting difficulties. With the capability of controllable DEP forces and the high sensitivity, this dielectrophoretic method is proved to be an effective technique for the manipulation of the high-throughput emulsion droplets in the microchannel [58]. However, there is few research on the dielectrophoretic behaviors of the IL-in-water emulsion droplets. It is highly desirable to study the dielectrophoretic behaviors of the IL-in-water emulsion droplets and the manipulation of the IL droplets under DC electric fields in the microchannel.

In this work, an asymmetric orifice based microfluidic chip is employed to investigate the dielectrophoretic behaviors of the IL-in-water emulsion droplets under DC electric field. The fabrication of the asymmetric orifice based microfluidic chip and the electric field distribution near the asymmetric orifice region were presented. Then, the DC dielectrophoretic behaviors of two different kinds of hydrophobic IL-in-water microemulsion droplets were investigated. By controlling the electrical conductivity of the suspending media, the positive and negative DEP behaviors of the IL microemulsion droplets were demonstrated and discussed and the separation of these two kinds of IL droplets of similar size was shown. Furthermore, the size-dependent separation of the IL droplets was conducted. This paper presents DC-DEP manipulation of the IL-in-water emulsion droplets by size and by kind for the first time, offering a strategy to manipulate the IL emulsion droplets and widening the DC-DEP applications in colloid and interface science.

2. Materials and methods

2.1. DC-dielectrophoresis

Dielectrophoresis is the movement of the polarizable particles or droplets suspending in a dielectric solution with a non-uniform electric field applied. Generally, the DEP forces exerting on the particles or droplets are given by [59]

$$F_{DEP} = 2\pi\varepsilon_m a^3 \,\mathrm{Re}\left(f_{CM}\right)\left(\nabla|E|^2\right) \quad (1)$$

where a represents the radius of the droplets, ε_m represents the electric permittivity of the dielectric medium, $\nabla|E|^2$ refers to the gradient of the square of the electric field, and $\mathrm{Re}\left(f_{CM}\right)$ describes the real part of the Clausius-Mossotti (CM) factor and is given by

$$f_{CM} = \left(\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*}\right) \quad (2)$$

$$\varepsilon^* = \varepsilon - \left(j\sigma/\omega\right) \quad (3)$$

where ε^* denotes the complex permittivity, the subscripts p and m represent the droplet/particle and the surrounding media, respectively. ε and σ are the permittivity and electrical conductivity, respectively. ω demonstrates the angular frequency of the AC electric fields. $j = \sqrt{-1}$. When the DC electric field is employed, the f_{CM} becomes soleyly dependent on the electrical conductivity of the droplet/particle σ_p and the surrounding solution σ_m, which is defined as [60]

$$f_{CM} = \left(\frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}\right) \quad (4)$$

The f_{CM} illustrates the relative polarizabilities of the droplet/particle and the surrounding media. The value of the